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**Procedure for the Determination of Acrolein and Other
Volatile Organic Compounds (VOCs) In Air Collected In
Canisters and Analyzed By Gas Chromatography/Mass
Spectrometry (GC/MS)**

Work Assignment 5-03

Prepared for:
Office of Air Quality Planning and Standards
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DISCLAIMER

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Standard Operating Procedure for the GC/MS Analysis of Acrolein in Canister Air Samples

1.0 IDENTIFICATION AND PURPOSE

The purpose of this document is to define the procedure for the analysis of acrolein simultaneous with other volatile organic compounds (VOCs) in ambient air canister samples. Acrolein has become a compound of interest, yet has proven difficult to analyze consistently. Using Method TO-15, along with this procedure, provides a consistent method for quantitating of acrolein.

This methodology may be applied to the analysis of canister air toxics samples introduced to a gas chromatograph/mass spectrometry (GC/MS) system using the selected ion mode (SIM) and a preconcentrator/autosampler. This analytical method can be used to quantify many VOCs, including acrolein with boiling points less than 200 °C.

2.0 MATRIX OR MATRICES

This SOP is applicable to ambient air, indoor air, landfill gas, and any air samples where VOCs are not present at levels above hundred of parts per billion volume (ppbv).

3.0 METHOD DETECTION LIMIT

Method detection limits (MDLs) for this canister analysis should be experimentally determined once a year. The detection limits are determined using the 40 CFR Part 136 Appendix B method of at least 7 replicates at 99% confidence level. It is possible to reach a detection limit of 0.05 ppbv for acrolein using the SIM method.

4.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) provides a method for the analysis of acrolein along with other VOCs in canister air samples by gas chromatography/mass spectrometry (GC/MS) in the SIMS mode with a preconcentrator and an autosampler (optional). The analysis of gaseous air samples from canisters is restricted to use by, or under the supervision of, analysts experienced in the use of GC/MS systems, skilled in the interpretation of mass spectra and their use as a quantitative tool, and skilled in performing qualitative and quantitative gas chromatographic analysis.

The method is applicable to ambient air, indoor air, landfill gas, and any air samples

where volatile organic analytes are not present at levels above hundred of ppbv. The methodology is not directly applicable to samples from combustion processes. A modifications of the methodology to allow direct gaseous injection or diluted canister gas analysis of air samples that contain high levels of organic compounds must be validated before use.

5.0 METHOD SUMMARY

Air samples are received in the laboratory in canisters. Appropriate gaseous calibration standards are prepared. The instrument is tuned and the range of calibration standards is analyzed. A calibration curve is obtained by response factor using internal standards. After the initial or daily calibration, a zero air sample containing purified humid air is analyzed before sample analysis. The quantities of acrolein and other analytes in the sample are calculated from the GC/MS response factors and reported. If verification of peak identity is needed, enhanced mass spectra are searched against the National Institute for Standards and Technology (NIST) reference library, and the data are interpreted by an experienced mass spectroscopist.

6.0 DEFINITIONS

amu	atomic mass units
BFB	1,4-bromofluorobenzene
CFR	Code of Federal Regulations
GC/MS	gas chromatograph/mass spectrometer
EPC	electronic pressure control
IS	Internal Standard
LCS	laboratory control sample
m	meter(s)
MB	megabyte(s)
MDL	method detection limit(s)
mL	milliliter(s)
mL/min	milliliter(s) per minute
mm	millimeter(s)
μL	microliter(s)
μm	micrometer(s)
MSD	mass selective detector
NIST	National Institute for Standards and Technology
NMOC	nonmethane organic compound
PFTBA	perfluorotributylamine
ppbC	parts per billion as Carbon
ppbv	parts per billion volume

psi	pounds per square inch
QA	quality assurance
QC	quality control
RF	response factor
RPD	relative percent deviation
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
sccm	standard cubic centimeter(s) per minute
sec	second(s)
SD	standard deviation
SOP	standard operating procedure
VOC	volatile organic compound

7.0 INTERFERENCES

This analytical methodology is based upon identification of and quantification of compounds using characteristic ions of the mass spectra, the comparison to reference spectra, and comparison to a retention time that is accurately known. Any elements of the air matrix that might interfere with the ability to identify the mass spectra, obtain accurate peak areas, or obtain an accurate retention time that can be compared with a reference standard will affect the performance of the analysis. If intense interfering peaks are encountered, the chromatography will be distorted. The solution to the problem of excessive compound loading is dilution of the sample or analysis of a smaller volume. If a coeluting compound is encountered, the characteristic mass fragments allow resolution unless the coeluting compound is an isomer of the compound of interest and the mass fragments are the same. In this case, within the limits of the present methodology, the problem cannot be resolved.

8.0 SAFETY

Standard safety procedures for the laboratory should be specified by each laboratory. The use of the GC/MS system and the preconcentrator requires attention to electrical hazards and hot surfaces. A MS analyst must be appropriately trained before using the instrumentation.

Any adjustment, maintenance or repair of the opened instrument while it is connected to a power source should be avoided if possible and, if required, should be carried out only by trained persons who are aware of the hazards involved.

9.0 EQUIPMENT

Automated Preconcentrator and Autosampler (autosampler is optional): Designed to interface between the sample in a canister and the chromatographic analytical system. A concentrator is a device for concentrating the condensable (organic) portion of an air sample. The system is usually controlled by vendor supplied software.

Gas Chromatograph/Mass Spectrometer System

- **Gas Chromatograph:** An analytical system complete with a temperature-programmable gas chromatograph with subambient capabilities and all required accessories, including gases, analytical columns, and separator.
- **Chromatographic Column:** DB-1 megabore fused silica capillary or equivalent, 60 meters (m) length × 0.32 milliliters (mm).
- **Mass Spectrometer:** Capable of scanning from 15 to 350 atomic mass units (amu) every 1 second (sec) or less, using 70 volts (nominal) electron energy in the electron ionization mode and producing a mass spectrum that meets all criteria for the manufacturer's specifications for perfluorotri-butylamine (PFTBA) tuning.
- **Analytical Data System Software:** The data system software includes programs to calibrate (tune the MSD), acquire data, and process data, as well as utilities for file management and editing. Tuning programs can adjust voltages in the ion source, calibrate mass assignments, and control the scanning of the mass analyzer. Data acquisition programs monitor the total ion current, automatically monitoring the concentrations of particular ions (selected ion monitoring mode). The data system also includes a mass spectral reference library for identification of mass spectra.

Bubble Flow Meter or other flow-measuring device.

10.0 MATERIALS

Liquid Nitrogen coolant for the GC/MS system and the preconcentrator, 22 psi.

Helium carrier gas for the GC/MS system, ultra high purity.

Sweep Purge Gas for the preconcentrator, Helium or clean dry Air.

11.0 CHEMICALS, REAGENTS, AND STANDARDS

Analytical standards can be prepared in the laboratory in canisters at the appropriate dilution from purchased standard mixture gas cylinders. A concentration of 0.5-1 ppm is the recommended for dilution from cylinder preparation of analytical standards. Method TO-15 provides the necessary guidance for dilution of standards. Analytical standards can also be used directly from purchased standard mixture gas cylinders. A standard from a secondary source should be obtained to used as a calibration check once a month.

12.0 COLLECTION, PRESERVATION, SHIPMENT, AND STORAGE

Ambient air samples are received in the laboratory in canisters. The canisters can be stored in the laboratory for up to 30 days until analysis.

13.0 CALIBRATION AND STANDARDIZATION

13.1 Initial Calibration

13.1.1 An initial calibration curve of at least 5 levels must be prepared from canister standards or standard mixture gas cylinders. The calibration range should encompass the expected sample concentration (example, approximately 0.5, 1, 5, 10, and 15 ppbv) for acrolein and each other compound of interest.

13.1.2 The data for the toxics calibration samples are updated into the data base and a complete response factor report can be generated in the data software. The percent relative standard deviation (%RSD) for each compound must be less than or equal to 30% RSD. See Table 24.2 for complete calibration criteria.

13.2 Internal Standards

The internal standards used can be purchased as standard mixture gas cylinders. Concentrations for the Internal Standards should be near the mid-point of the initial calibration analysis. Internal Standards are loaded by the preconcentrator with every standard, zero air, and sample analyses.

14.0 PROCEDURE

14.1 Preparation of the Gas Chromatograph

- 14.1.1 Install the transfer lines from the preconcentrator to the GC. These lines may be deactivated stainless steel (SilcoSteel[®]) tubing housed in a heated transfer line. Insert one side of a stainless steel line through the base of the GC injector and the other side into the preconcentrator. With this arrangement, syringe injections can be made without plumbing changes. Refer to the preconcentrator and GC/MS operators manuals for complete installation instructions.
- 14.1.2 The transfer line through the GC injector is now connected to the analytical column. A connection is made with a low dead volume connector.
- 14.1.3 Attach the other end of the column to the MS detector following the instructions in the GC/MS operators manual.
- 14.1.4 Set the column (helium) carrier flow to 1.0 mL/min. GC models equipped with an EPC should be set following the instructions in the GC/MS operators manual.
- 14.1.5 Allow the GC time to purge the ambient air from the instrument before ramping the GC oven above 100 °C.
- 14.1.6 The following instrument conditions are used on the GC/MS system.

MS Information

Solvent Delay:	4.0 min
EM Absolute:	True
Resulting Voltage:	2000 (usually set approximately 200 above the autotune)
[SIM Parameters for acrolein]	
Scan Group ID:	#
Resolution:	Low
Group Start Time:	14.0
Plot 1 Ion:	56.0
Ions/Dwell Time In Group:	(56.0, 30) (55.0, 30)

GC Temperature Information

Initial Temp:	-30°C
Initial Time:	5.00 min

Level	Rate (°C/min)	Final Temp (°C)	Final Time (min)
1	15.00	0	0.00
2	5.00	150	0.00
3	25.00	250	6.20
Next Run Time:		48.53 min	

Timed MS Detector Entries

Time (min)	State (MS on/off)
44.00	Off

14.2 Preparation of the Preconcentrator

A microscale purge and trap method configuration is used to preconcentrate the samples for analysis. The microscale purge and trap methods are analogous to purge and trap used in water analysis, only on a much smaller scale. The air sample is first trapped cryogenically (at -150 °C) onto a hybrid glass bead trap/Tenax® to concentrate the volatile organic compounds, CO₂, and H₂O into roughly a 0.5-mL volume. The trap is then heated to room temperature and is held there while helium slowly passes through it to transfer the VOCs to a second trap. The second trap contains Tenax® and is held at -30 °C to retain the VOCs transfer from the first to the second trap with only 75 mL of sweep/purge gas. The MS can handle this quantity of water quite easily (< 0.5 microliter (µL)). After the microscale purging and trapping, the second trap is heated to 120 °C and back flushed to the focusing trap and held at -160 °C to allow a rapid injection of the VOCs onto the analytical column.

Since the water is left behind in the primary trap (and later baked out), this technique has no inherent sample volume limitation. Typical sample volumes using the 1/8-in. module glass bead trap are from 400 to 600 mL.

One method is used for all standards and samples to be analyzed. The preconcentrator method has the following set points (the type of preconcentrator may vary):

NOTE: To ensure that the GC oven will be at proper temperature during the injection of sample, it may be necessary to start the preconcentrator before starting the GC/MS.

14.3 Data Analysis/QA/QC

14.3.1 **BFB Tune:** Perform a bromofluorobenzene (BFB) tune at the beginning of each 24-hour GC/MS analysis time period to demonstrate that the tuning performance criteria have been met before the initiation of any sample analyses.

14.3.2 **Reporting Quality Assurance (QA)/QC Reports from the Preconcentrator Software:** After all of the samples have been analyzed, the QA/QC report needs to be retrieved from the preconcentrator software. The QA/QC report will list the critical parameters obtained during the concentration process. Most instrument problems can be resolved by close examination of the parameters on the report.

14.3.3 **Reprocessing Data in the Analytical Data System Software:** The Data System Software program allows you to correct and display data acquired by a mass spectrometer. You can use data analysis to integrate chromatograms, generate ion chromatograms, generate and review reports, and edit spectral data.

14.4 Daily Analysis

14.4.1 A calibration standard should be used as a quality check daily before the initiation of sample analysis to ensure that the response factor generated in the initial calibration is still valid. The standard should be at a concentration in the mid-range of the initial calibration curve. A second source calibration check standard is used to verify the original calibration at least once per month.

14.4.2 With updated compound concentrations and analyses responses for the mid-level standard in the data software, the report will give the average response factors from the current curve, the daily calibration response factors, % deviation, area %, and deviation in minutes. In order for the daily calibration to be valid, the % deviation for all compounds must be within 30% of the initial curve.

If the daily calibration check standard analysis is outside these specifications, analyze another daily calibration check sample. If specifications are not met upon reanalysis of the daily check sample, a new multipoint calibration curve must be generated or system maintenance must be performed. See Table 24.2 for complete calibration criteria.

14.4.3 Analyze a zero air canister containing purified, humidified air to prove that

the analytical system is clean. A clean zero air blank of <0.2 ppbv of acrolein or any target compound, must be obtained before the initiation of any sample analysis.

14.4.4 In the data software, quantify each analytical sample for acrolein and other toxics compounds against the curve. Verify the identification of acrolein and any other target analytes by evaluating the identification and integration of the peaks. Following the conditions stated in this procedure, acrolein should be at approximately 14.79 minutes retention time with ions 56 and 55.

14.4.5 The internal standard responses for each standard, zero air, and sample analyzed must be within 40% of the internal standard responses of the daily calibration. In environmental data analysis, this can be done automatically as in Table 24.1.

14.4.6 The sequences for the MS always end with a method to allow the column to bake out over any length of time that the GC/MS is not analyzing samples.

15.0 CALCULATIONS

Calculations are performed in the data system; the equations shown below are used.

15.1 Response Factor (RF)

The RF is calculated as follows:

$$RF = [A_s \times C_{is}] / [A_{is} \times C_s]$$

Where:

A_s = Peak area for the characteristic ion of the analyte

A_{is} = Peak area for the characteristic ion of the internal standard

C_s = Concentration of the analyte

C_{is} = Concentration of the internal standard.

15.2 Standard Deviation (SD)

The SD is calculated as follows:

$$SD = \sqrt{\sum_{i=1}^n (RF_i - \overline{RF})^2 / n - 1}$$

Where:

RF_i = RF for each of the calibration compounds

\overline{RF} = mean RF for each compound from the initial calibration

n = number of calibration standards

15.3 Relative Standard Deviation (RSD)

The RSD is calculated as follows:

$$RSD = (SD/\overline{RF}) \times 100$$

Where:

SD = standard deviation

\overline{RF} = mean RF for each compound from the initial calibration

15.4 Relative Percent Difference (RPD)

The RPD is calculated as follows:

$$RPD = (|R_1 - R_2|) / [(R_1 + R_2)/2] \times 100$$

Where:

R_1, R_2 = values that are being compared (i.e., response factors in calibration verification)

16.0 QUALITY CONTROL

16.1 Method QC Checks

The QC checks listed below are used to assure the production of data of known quality by the analytical method. Table 24.2 presents a complete QC objective.

16.1.1 Calibration Criteria

For samples analyzed for toxics compounds, a 5-point calibration is performed initially for each method, and a response factor is determined from the calibration data points. A percent deviation of 30% or better must be obtained for acrolein and other target analytes. If the response factor is greater than 30% for any of the analytes, additional calibration samples are analyzed until the criteria are met.

16.1.2 Tuning Criteria

The GC/MS instrument is tuned according to Method TO-15 criteria for BFB, with the following mass assignments:

Target Mass	Rel. To Mass	Lower Limit %	Upper Limit %
50	95	15	40
75	95	30	60
95	95	100	100
96	95	5	9
173	174	0	2
174	95	50	100
175	174	5	9
176	174	95	101
177	176	5	9

16.1.3 Daily Calibration Check

A daily calibration check at a varied calibration range is performed before the initiation of any quantitative analyses. The amounts for the calibration check are generated in the data system by response factor. Percent deviation is calculated from the calibration curve ($\pm 30\%$). If this criterion cannot be met, an additional daily calibration check sample is analyzed. If the criterion still cannot be met, a new multipoint calibration is generated.

16.1.4 Analysis of Zero Air Samples

No target analytes should be observed in zero air samples at levels higher than three times the method detection limits or 0.2 ppbv. If these criteria are not met, a new zero air sample is analyzed until a clean blank is obtained. The zero air sample analysis is performed after the calibration check analysis and before the initiation of any quantitative analyses.

17.0 PREVENTION

N/A

18.0 CORRECTIVE ACTION

Corrective action for any VOC analyses data quality issues should be developed by each laboratory. Table 24.2 gives the data quality guidelines and the associated recommended corrective actions.

19.0 WASTE MANAGEMENT

N/A

20.0 MAINTENANCE

The trained GC/MS analyst can perform routine maintenance, including changing columns, changing filaments, cleaning ion sources, and changing the electron multiplier as required. Some MS maintenance may require a contracted MS service technician. Routine maintenance for the preconcentrator includes changing the sample traps, and leak-checking the autosampler.

All maintenance activities should be documented in the instrument maintenance logs.

21.0 SHORTHAND PROCEDURE

The flow chart shown in Figure 24-1 shows the procedural steps for analysis of canister samples.

22.0 DOCUMENTATION AND DOCUMENT CONTROL

22.1 Preparation of the Project Data File

All data associated with instrument tuning, calibration, and analyses can be compiled into a project file. The following is typical information that can be collected into the project file:

- 1) **Canister Information:** The chain of custody sheets and any other notes or comments relating to the canisters become a part of the project data file.
- 2) **Standards Information:** If analytical standards are prepared by the laboratory, a data sheet that lists the compounds and concentrations for each canister standard should be generated and included in the project file. If purchased cylinders are used, a copy of the certificate of analysis should be included in the project file.
- 3) **Tuning Data:** The instrument is required to show that tuning criteria have been met before the initiation of any analyses. The tuning data for the mass spectrometer include a mass spectrum of BFB and a list of the tabulated masses of the compound. See Section 16.1.2.
- 4) **Calibration Data:** For each analysis of the calibration, a chromatogram and the output of the data system listing areas of peaks for each of the target analytes are included. The inclusion of the raw data for the calibration will allow a reviewer or another analyst to reconstruct the linear regression.
- 5) **Zero Data:** For each of the purified humid air samples analyzed, a chromatogram and the output of the data system are included in the project file. If any analytes are identified in these zero air samples, a mass spectrum and the calculated quantity are supplied.
- 6) **Sample data with mass spectra for all targets:** For each of the canister samples, an enhanced mass spectrum is included in the data folder for each analyte. A chromatogram for each sample is also included, the hard copy from the data system that includes quantitation peaks for the analytes identified, a peak area for the major ion, and a retention time.
- 7) **Calculation sheet, if any manual calculations are performed:** Quantitative calculations for the target analytes identified are performed by the computer using the response factor generated in the analysis of the calibration samples. If any additional calculations are necessary, a

calculation sheet is included to demonstrate how the calculations are performed. The necessary calculations are actually performed and the results written directly onto the data sheets.

- 8) **Reporting Quality Assurance (QA)/QC Reports from the Preconcentrator Software:** The QA/QC report will list the critical parameters obtained during the concentration process.

22.2 Analysis Logbook

The following is typical information to record in an analysis logbook:

- 1) The sample ID and the field ID are listed with the names that correspond to the chain of custody report.
- 2) Any sample identification number assigned by the laboratory.
- 3) Each analysis must be assigned a unique file name that unambiguously designate the instrument on which the sample was analyzed.
- 4) The date of the sample collection.
- 5) The date of the analysis is recorded in the analysis logbook. The time of the analysis is available from the data file.
- 6) If the sample analyzed is a standard, the standard reference number is recorded in the analysis logbook. If the sample is not a standard, 'NA' is entered into the logbook.
- 7) The method used to acquire MS data.
- 8) The amount of sample loaded by the autosampler.
- 9) The sample can number.
- 10) The initials of the analyst.
- 11) Any appropriate comments relative to the analysis.

22.3 Maintenance Logbook

All instrument maintenance is documented in a maintenance logbook dedicated to the instrument.

23.0 REFERENCES

Compendium of Methods for the determination of Toxic Organic Compounds in Ambient Air. Second Edition Compendium Method To-15. Determination of Volatile Organic Compounds (VOCs) in air collected in specially prepared canisters and analyzed by gas chromatography/mass spectrometry (GC/MS). EPA-625/R-96/0106. US Environmental Protection Agency. 1999.

24.0 TABLES, DIAGRAMS, FLOW CHARTS, VALIDATION DATA

Table 24-1. Supporting Data for Internal Standard

3/18/2004	7:37	L4CR001.D	IS-HEXANE-d14	859471
3/18/2004	8:47	L4CR002.D	IS-HEXANE-d14	852726
3/18/2004	1:24	L4CR003.D	IS-HEXANE-d14	867123
3/18/2004	2:35	L4CR004.D	IS-HEXANE-d14	876896
3/18/2004	3:46	L4CR005.D	IS-HEXANE-d14	894706
3/18/2004	4:57	L4CR006.D	IS-HEXANE-d14	885857
3/18/2004	6:07	L4CR007.D	IS-HEXANE-d14	769423
3/18/2004	7:18	L4CR008.D	IS-HEXANE-d14	776722
3/18/2004	8:30	L4CR009.D	IS-HEXANE-d14	758223
3/18/2004	9:41	L4CR010.D	IS-HEXANE-d14	748980
3/18/2004	10:52	L4CR011.D	IS-HEXANE-d14	867440
3/19/2004	12:03	L4CR012.D	IS-HEXANE-d14	752114
3/19/2004	1:14	L4CR013.D	IS-HEXANE-d14	862808
3/19/2004	2:25	L4CR014.D	IS-HEXANE-d14	850785
3/19/2004	3:36	L4CR015.D	IS-HEXANE-d14	854073
3/19/2004	4:47	L4CR016.D	IS-HEXANE-d14	841303
3/19/2004	5:58	L4CR017.D	IS-HEXANE-d14	855694
3/19/2004	7:09	L4CR018.D	IS-HEXANE-d14	854510

IS Limits

515683 1203259

Figure 24-1. Flow Chart for GC/MS Air Toxics Analysis

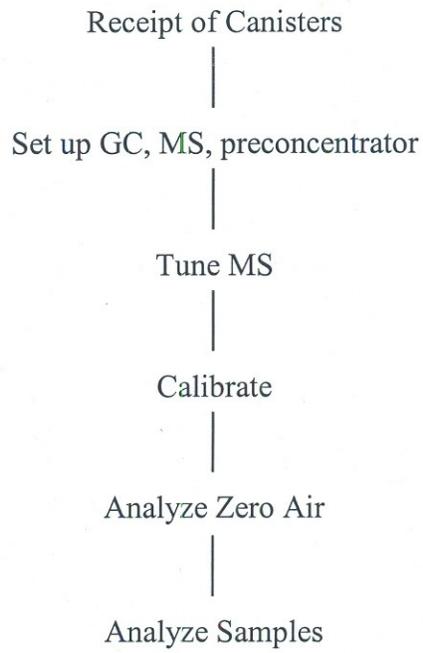


Table 24-2. Data Quality Objectives

QC Check	Frequency	Acceptance Criteria	Corrective Action
Bromofluorobenzene (BFB) Instrument Tune Performance Check	Daily, prior to sample analysis	Evaluation criteria in Section 16.1.2 presented in this SOP.	<ol style="list-style-type: none"> 1) Retune 2) Clean ion source and/or quadrupoles
Multipoint (at least five) calibration bracketing the expected sample concentrations.	Following any major change, repair or maintenance or if daily QC is not acceptable. Recalibration not to exceed three months.	<ol style="list-style-type: none"> 1) RSD of response factors $\leq 30\%$ 2) Relative Retention Times (RRTs) for target peaks ± 0.06 units from mean relative retention time 	<ol style="list-style-type: none"> 1) Repeat individual sample analysis 2) Repeat calibration curve 3) Prepare new calibration standards and repeat analysis
Calibration check using midpoint of calibration curve or one other point in curve.	Daily, prior to sample analysis	Analyst verifies that the response factor $\leq 30\%$ bias from calibration curve average response factor	<ol style="list-style-type: none"> 1) Repeat calibration check 2) Repeat calibration curve
LCS (Second Source Standard)	Monthly	Analyst verifies that the recoveries are 70% - 130%	<ol style="list-style-type: none"> 1) Repeat analysis 2) Repeat calibration
System Blank Analysis	Daily following BFB and calibration check; prior to sample analysis	<ol style="list-style-type: none"> 1) < 0.2 ppbv per analyte 2) Internal Standard (IS) area response $\pm 40\%$ and IS Retention Time (RT) ± 0.33 min. of most recent calibration check 	<ol style="list-style-type: none"> 1) Repeat analysis with new blank canister 2) Check system for leaks, contamination 3) Reanalyze blank
Duplicate and Replicate Analysis	All duplicate field samples	$< 30\%$ RPD for compounds greater than 5 times MDL	Repeat sample analysis
Samples	All samples	IS area response $\pm 40\%$ of calibration mean and IS retention time ± 0.33 min of calibration	Repeat analysis